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(56) Documents cited

GB 1430453	GB 1293111	EP A2 0022618
GB 1381008	GB 1154191	WO A1 8200532
GB 1310812		

(58) Field of search

G2C

(54) Optical recording medium

(57) An optical recording medium and an optical recording process using such a medium are provided. The optical recording medium comprises a photo-polymerizable monomer having a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule. Preferably the or each monomer is arranged in one or more molecular layers having common orientation. Preferred monomers have both hydrophilic and hydrophobic groups and contain a C<sub>12</sub> to C<sub>30</sub> alkyl groups.

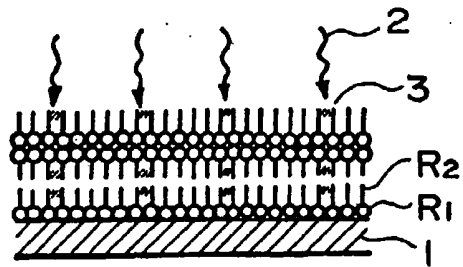


FIG. 1

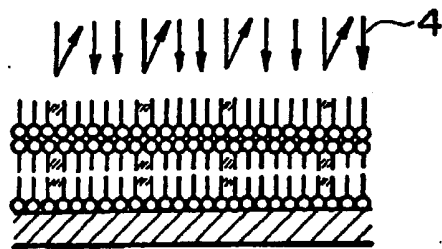


FIG. 2

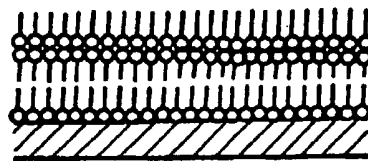


FIG. 3

## SPECIFICATION

## Optical recording medium and optical recording process using such medium

## 5 BACKGROUND OF THE INVENTION

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*Field of the Invention*

The present invention relates to an optical recording medium which comprises a photopolymerizable monomer and to an optical recording process using such a medium.

## 10 Description of the Prior Art

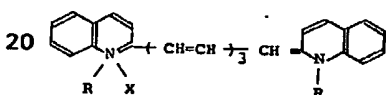
10

There have so far been known optical recording media which comprise films as recording layers formed from organic compounds; for example, such media are disclosed in Japanese Patent Application Laid-Open Nos. 16,948/81 and 125,246/83. Both of the disclosures relate to a recording media having a recording layer composed of an organic coloring matter for

## 15 recording and reproducing information by use of laser beams.

15

The medium disclosed in the latter patent application laid-open gazette employs a recording layer formed from cyanine coloring matter represented by the general formula



20

The recording layer is formed by applying a solution of the coloring matter in the thickness of up to 1000 Å, for example, about 300 Å, on a plastic substrate using a spinner coater or the like. When the molecular distribution or orientation in the layer is random, the incident light scatters in the layer and the extent of chemical reaction caused by light irradiation varies microscopically at every irradiation. In consequence, for recording media, the molecular distribution and orientation in the layer is desired to be uniform and the layer thickness is required to be minimized for the purpose of obtaining high-density recording. By coating methods, however, the lower limit of the layer thickness is about 300 Å and the random molecular distribution and orientation are inevitable.

Meanwhile, Japanese Patent Application Laid-Open Nos. 42,229/81 and 43,220/81 disclose that a built-up film of a diacetylene compound formerly proposed as one of resist materials that shows a high light quantum yield and has a superior resolution can also be applied to thin film electrooptic devices, electro-acoustic devices, and piezoelectric and pyroelectric devices, etc.

Recently an improved process for producing built-up films of diacetylene compounds is disclosed in Japanese Patent Application Laid-Open No. 111,029/83. Built-up films of diacetylene compounds produced according to these inventions are used for film-optic devices and integrated circuit elements, after the polymerisation thereof by ultraviolet irradiation to form a polymer film or partial polymerisation thereof by ultraviolet irradiation under masking and pattern formation by removing the unpolymerised portions.

However, these patent applications are all limited to diacetylene compounds and do not describe the possibility of erasing information once recorded when built-up films of a diacetylene compound are used for film-optic devices.

The primary object of the invention is to provide an optical high-density-recording medium which permits repetition of recording and erasing of information.

Another object of the invention is to provide an optical recording process using such a recording medium.

According to one aspect of the invention there is provided an optical recording medium comprising one or more distributed photopolymerisable monomers arranged to produce an erasable, image-readable pattern of localised polymer areas upon image-wise irradiation.

Preferably, the or each monomer is arranged in one or more monomolecular layers, and more preferably the molecules in each layer have a common orientation.

The preferred monomers each comprise a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule.

The invention includes a process in which the recording medium comprises one or more distributed photopolymerisable monomers and in which image-wise irradiation induces a polymerisation reaction in the irradiated areas leading to the detectable localised presence of polymer.

According to another aspect of the present invention, there is provided an optical recording process which uses a recording medium comprising a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule.

According to another aspect of the present invention, there is provided an optical recording

medium comprising a recording layer which is a monomolecular film or built-up film of monomolecular layers formed on a substrate, of a photopolymerisable monomer having a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule.

- 5 According to further aspect of the present invention, there is provided an optical recording medium comprising a recording layer which is a built-up film of monomolecular layers formed on a substrate, of two or more kinds of photopolymerisable monomer having a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule respectively. 5

Figure 1 is an illustration showing a preferred form of recording layer of photopolymerisable monomer in the recording state of the optical recording medium according to the invention.

- 10 Figure 2 is an illustration showing the recording layer in the state of reading out recorded information. 10

Figure 3 is an illustration showing the recording layer from which the recorded information is erased.

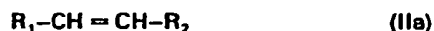
- The preferred form of optical recording medium comprises a recording layer which is a 15 monomolecular film or built-up film of monomolecular layers formed of one or more kinds of photopolymerisable monomers on a substrate. 15

- In the preferred form of the invention, the photopolymerisable monomer is applied to a substrate in the form of a monomolecular film or a built-up film of monomolecular layers on a substrate. The molecules of the film are preferably polarised, i.e., they have a common 20 orientation. These films can be used as recording layers for optical recording. 20

- In the optical recording medium of the invention, recording is accomplished by irradiating the photopolymerisable monomer of the recording layer with light signals of information to polymerise the irradiated portion of the monomer, thus forming a difference due to the polymerisation between the irradiated and unirradiated portions. The reproduction can be carried 25 out by various methods for measuring the difference caused by the polymerisation. Further erasing of the recorded information is carried out by heating to depolymerise the polymer. 25

A wide variety of photopolymerisable monomers can be used as the compounds for optical recording media in the invention, so long as they have (in the preferred case) a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule.

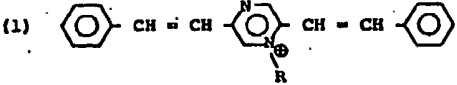
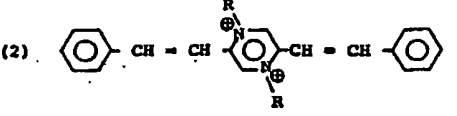
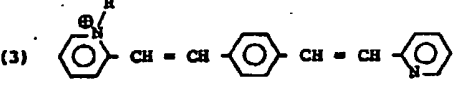
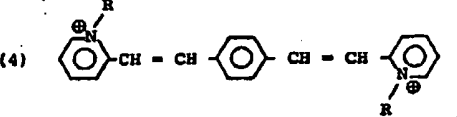
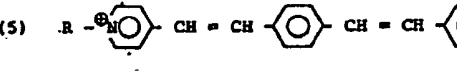
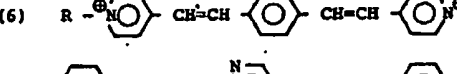
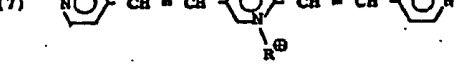
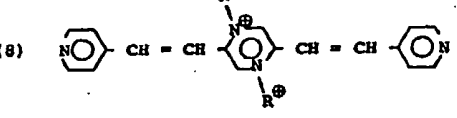
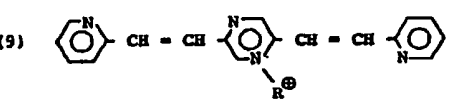
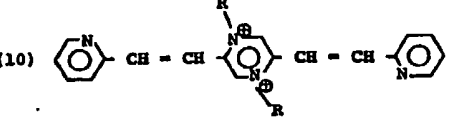
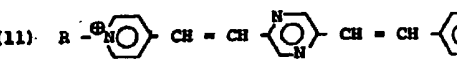

- 30 These photopolymerisable monomers can be represented by the general formula (IIa), (IIb), or (III): 30

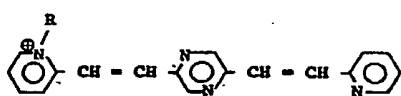
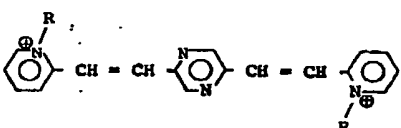
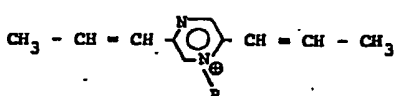
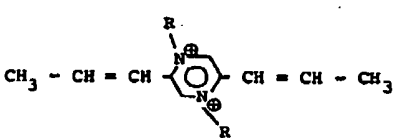
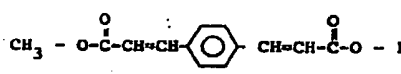
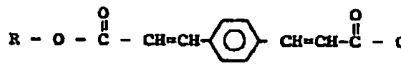
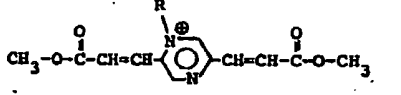
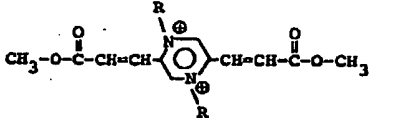
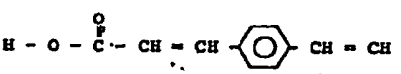
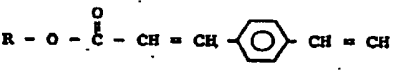
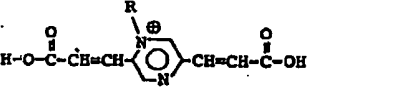
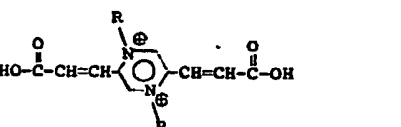
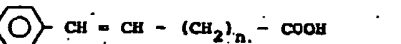


- 35  $R_1-C\equiv C-C\equiv C-R_2 \quad (III)$  35

- In the formulae (IIa) and (III), a hydrophilic site and a hydrophobic site are both present in  $R_1$  or in  $R_1$  and  $R_2$ , or  $R_1$  is hydrophobic relative to  $R_2$ , that is,  $R_2$  is hydrophilic relative to  $R_1$ . In the formula (IIb), a hydrophilic site and a hydrophobic site are both present in one of  $R_1$ ,  $R_2$ , 40 and  $R_3$  or one of  $R_1$ ,  $R_2$ , and  $R_3$  is hydrophobic relative to the remainders and one of the remainders is hydrophilic. Particularly preferred photopolymerisable monomers in the invention have a  $C_{10}$ - $C_{20}$  long chain alkyl group in  $R_1$ , such two alkyl groups in  $R_1$  and  $R_2$  respectively, or 40 such an alkyl group in at least one of  $R_1$ ,  $R_2$ , and  $R_3$ .

Examples of the preferred photopolymerisable monomers of the invention are given below.

- (1)   $\cdot X^{\ominus}$
- 5
- (2)   $\cdot 2X^{\ominus}$
- 10
- (3)   $\cdot X^{\ominus}$
- 15
- (4)   $\cdot 2X^{\ominus}$
- 20
- (5)   $\cdot X^{\ominus}$
- 25
- (6)   $\cdot 2X^{\ominus}$
- 30
- (7)   $\cdot X^{\ominus}$
- 35
- (8)   $\cdot 2X^{\ominus}$
- 40
- (9)   $\cdot X^{\ominus}$
- 45
- (10)   $\cdot 2X^{\ominus}$
- 50
- (11)   $\cdot X^{\ominus}$
- (12)   $\cdot 2X^{\ominus}$

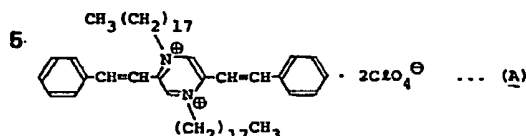
- (13)   $\cdot X^{\ominus}$
- 5
- (14)   $\cdot 2X^{\ominus}$
- 10
- (15)   $\cdot X^{\ominus}$
- 15
- (16)   $\cdot 2X^{\ominus}$
- 20
- (17)   $\cdot X^{\ominus}$
- 25
- (18)   $\cdot X^{\ominus}$
- 30
- (19)   $\cdot X^{\ominus}$
- 35
- (20)   $\cdot 2X^{\ominus}$
- 40
- (21)   $\cdot X^{\ominus}$
- 45
- (22)   $\cdot X^{\ominus}$
- 50
- (23)   $\cdot X^{\ominus}$
- 55
- (24)   $\cdot 2X^{\ominus}$
- 60
- (25)   $\cdot X^{\ominus}$

- (26)  $\text{HOOC}-(\text{CH}_2)_n-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-(\text{CH}_2)_n-\text{COOH}$
- 5 (27)  $\text{R}-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}-\text{C}(\text{CN})(\text{COOCH}_2\text{CH}_3)$  5
- 10 (28)  $\text{N}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{N}^+(\text{R})\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5) \cdot \text{X}^-$  10
- 15 (29)  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{N}^+(\text{R})\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_5 \cdot \text{X}^-$  15
- 20 (30)  $\text{R}-\text{N}^+(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5) \cdot \text{X}^-$  20
- (31)  $\text{R}-\text{N}^+(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{N}^+(\text{C}_6\text{H}_5)-\text{R} \cdot 2\text{X}^-$  25
- 25 (32)  $\text{CH}_3-\text{CH}=\text{CH}-\text{N}^+(\text{R})\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}_3 \cdot \text{X}^-$  30
- 30 (33)  $\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{OR}$
- 35 (34)  $\text{R}-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{OR}$  35
- (35)  $\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{N}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{OR}$  40
- 40 (36)  $\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{N}^+(\text{R})\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{CH}_3 \cdot \text{X}^-$  45
- 45 (37)  $\text{HO}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{N}^+(\text{R})\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{OH} \cdot \text{X}^-$  50
- 50 (38)  $\text{CH}_3-(\text{CH}_2)_x-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_y-\text{COOH}$
- 55 (38)  $\text{CH}_3-(\text{CH}_2)_x-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_y-\text{COOH}$  55
- (x and y denote each 0 or a positive integer and satisfy  $10 \leq x + y \leq 30$ ).  
In the above formulas:  $\text{R} = -(\text{CH}_2)_n\text{CH}_3$
- 60  $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{ClO}_4^-, ^-\text{OSO}_2-\text{C}_6\text{H}_4-\text{CH}_3, ^-\text{OSO}_2-\text{C}_6\text{H}_4-\text{Cl},$  60

or the like; and n = a positive integer.

The above photopolymerizable monomers are themselves known compounds [described in "Kagaku to Kogyo (Chemistry and Chemical Industry)", 32, No. 10, pp. 763-765] or are 65 compounds analogous in structure thereto, except that long-chain alkyl groups are introduced

therein. Accordingly, these monomers can be synthesized according to known processes. For example, 1, 4-di-n-octadecyl-2, 5-distyrylpyrazine perchlorate,



10 which is a photopolymerizable olefin monomer having a  $C_{18}$  long chain alkyl group (n-octadecyl group) can be prepared in the following way:

10.8 g of 2,5-dimethyl pyrazine and 44.5 g of n-octadecyl p-chlorobenzenesulfonate are dissolved in 100 ml of DMF and heated under reflux for 1 hour in an atmosphere of nitrogen. After cooling, a solution of 10 g of sodium perchlorate in 200 ml of water is added. The solid deposit is washed with ether and recrystallized from methanol. 4.7 g of the thus obtained 1,4-di-n-octadecyl-2, 5-dimethyl pyrazine and 1.04 g of benzaldehyde are heated together in acetic anhydride under reflux for 3 hours. After cooling, A is obtained by recrystallization from methanol in a 40% yield. Other monomers of the invention can be prepared in similar ways.

20 The monomolecular film and the built-up film of monomolecular layers are formed according to, for example, the Langmuir-Blodgett's technique (LB method) developed by I. Langmuir et al. The LB method utilizes the fact that molecules having hydrophilic and hydrophobic groups in the molecule, wherein the lyophilic and lyophobic properties are suitably balanced, form a monomolecular layer on a water surface with hydrophilic groups thereof being directed downward. The monomolecular layer on a water surface has characteristics of a two-dimensional system. When molecules are sparsely scattered, there is the relation of two-dimensional ideal gas between the area A of the layer per one molecule and the surface pressure  $\pi$ .

$$\pi A = kT$$

30 wherein k is Boltzmann's constant and T is the absolute temperature of the molecules. Thus, the monomolecular layer is regarded as a "gaseous film". When the area A is decreased sufficiently, the molecular interaction is enhanced and the monomolecular layer becomes a "condensed film (or solid film)". The condensed film can be transferred layer by layer onto a substrate such as a glass plate. Using this method, the monomolecular film and the built-up film of monomolecular layers can be produced, for example, in the following way:

The photopolymerizable monomer is first dissolved in a solvent, and the solution is spread on a water surface to float the monomer in film form. In this case, a partition plate (or a float) is provided to restrict the free diffusion of the monomer on the water surface so as not to spread too far. Thus the aggregation state of the film-forming monomer is controlled to attain a surface pressure  $\pi$  proportional to the degree of the aggregation. The surface pressure  $\pi$  can be raised gradually to a suitable value for the formation of a built-up film by moving the partition plates to reduce the area of the spread monomer layer and controlling the aggregation state of monomer molecules in the layer. The monomolecular layer of the monomer can be transferred onto a clean substrate by a slow vertical movement thereof across the floating monomer layer while keeping the suitable surface pressure. The built-up film of monomolecular layers of the monomer having a desired built-up degree can be formed by repeating the above operation.

One or more kinds of molecules for constructing the film are selected from the above defined photopolymerizable monomers. When two or more photopolymerizable monomers are used, each monomolecular layer made of one kind of photopolymerizable monomer. Various combinations of monomolecular layers different in the kind of constituent molecule are possible for constructing the built-up film; for example, photopolymerizable monomers a and b can be built up in the sequence of (ab)<sub>n</sub>, (a<sub>m</sub>b<sub>l</sub>)<sub>n</sub>, or a(b)<sub>n</sub> (wherein n, m, and l are each a positive integer of 1 or more) from the substrate side or completely at random. The combination is chosen depending upon properties of the photopolymerizable monomers to be used and some other factors.

Suitable thicknesses of the recording layer are 30 Å–3 μm, particularly 100–3000 Å. Taking this into account, the photopolymerizable monomers to be used and the degree of built-up are chosen.

For transferring the monomolecular layer onto a substrate, the lifting method and the rotary cylinder method can also be applied besides the above vertical dipping method. The lifting method is a way of transferring a monomolecular layer onto a substrate by bringing the substrate into contact with a monomolecular layer on a water surface while keeping the substrate surface horizontal. The rotary cylinder method comprises rotating a cylindrical substrate on a monomolecular layer formed on a water surface, thereby transferring the monomolecular layer onto the substrate surface. In the vertical dipping method, the first

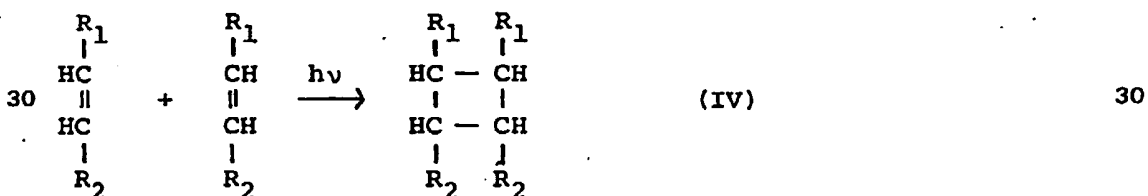


monomolecular layer, on raising a substrate across the water surface, is formed on the substrate with the hydrophilic groups facing the substrate. One monomolecular layer is deposited by each vertical movement of the substrate. Orientations of molecules in the monomolecular layers transferred by raising the substrate and by sinking it are in the directions opposite to each other.

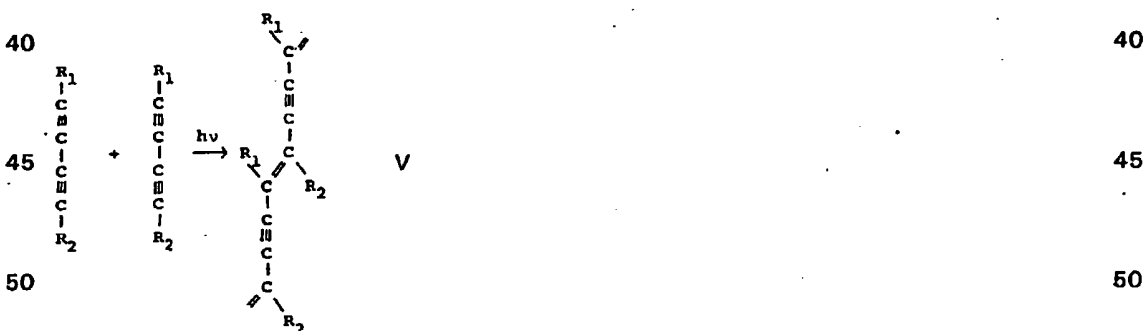
5 Accordingly, the vertical dipping method gives a so-called Y-type of film in which hydrophilic groups or hydrophobic groups face one another between each two adjoining layers. In contrast to this, the lifting method, the way of transferring a monomolecular layer from a water surface onto a substrate by horizontal contact thereof with the layer, forms on a substrate a monomolecular layer in which hydrophobic groups face the substrate. According to this method, 10 the alternate directional molecular orientation is not caused in the built-up film, and thus a so-called X-type of built-up film is formed, wherein hydrophobic groups in all the layers are directed toward the substrate. On the contrary, the built-up film wherein hydrophilic groups in all the layers are directed toward the substrate is called a Z-type of built-up film.

The rotary cylinder method is a way of transferring a monomolecular layer onto a cylindrical 15 substrate surface by rotating the cylindrical substrate on a monomolecular layer formed a water surface. The method for transferring the monomolecular layer onto the substrate in the invention is not limited to the above stated methods. When large area substrates are employed, a roll of substrate is unwound to push forward the continuous substrate into water on which the monomolecular layer of the monomer has been formed. The above said directions of hydrophilic 20 and hydrophobic groups, being merely in principle, can be changed by surface treatment of the substrate or other suitable methods.

On irradiation of the thus prepared optical recording medium with a pattern of light, such as  $\gamma$ -ray, X-ray, or ultraviolet ray, which is capable of supplying the energy necessary for the polymerization, the polymerization takes place as shown below in the irradiated sites when the 25 monomer is represented by the formula (IIa).



35 With a diacetylene compound represented by the formula (III), the polymerization takes place as shown by the following equation:



These reactions can be caused when the distance between adjacent unsaturated bonds is 4 Å 55 or less. That is, such a polymerization can take place between adjacent molecules in the same layer of the monomolecular film or of the built up film prepared as stated above as well as between adjacent molecules in adjacent layers facing each other of the built-up film. The polymer does not depolymerize in the dark and the monomer in the unirradiated sites remains unpolymerized. Thus, recording is accomplished in accordance with the pattern of light as 60 shown in Fig. 1.

Recorded information can be read out, for example, by visible ray irradiation. Since some conjugated bonds in the monomer are lost by the polymerization, a change has occurred in the visible ray absorption spectrum of the irradiated sites. That is, since the absorption maximum has shifted to the shorter wavelength side, the information is read out by measuring the change 65 in the absorption spectrum (Fig. 2). Therefore, a longer conjugation system will leads to a larger

difference in maximum absorption wavelengths between the monomer and the polymer, resulting in easier reproduction.

Recorded information can also be read out by observing, besides the change in the visible ray absorption spectrum, the volume change between the monomer and the polymer according to the schlieren method. This method is specially suited to monomolecular films of monomers in which a larger volume change is caused on polymerization. The reading of recorded information is also possible, when the monomolecular film or the built-up film of monomolecular layers is formed not directly on the substrate but on a photoconductive layer of Se, ZnO, or CdS formed on the substrate, by an electrical detection of the difference in light absorbance between the monomer and the polymer.

Erasing of recorded information is accomplished by heating the medium at a temperature, e.g. of 300–450°C, to depolymerize the polymer (Fig. 3). While this heating causes a degradation of the recording layer, the optical recording medium can be used repeatedly up to about 100 times.

The substrate on which the monomolecular film or the built-up film of monomolecular layer of the monomer is formed in the invention is not particularly limited. However, the surface of the substrate needs to be clean since a surface active substance adhering the substrate surface disorders the monomolecular film during the transfer thereof from a water surface, resulting in inferior monomolecular film or built-up film. Suitable materials for the substrate include, for example, glass, metals such as aluminum, plastics, and ceramics.

While the monomolecular film or the built-up film of monomolecular layers is sufficiently firmly fixed on the substrate and hence scarcely peels off the substrate, a bond layer can be laid between the substrate and the film for the purpose of more enhancing the adhesion. The adhesion can also be enhanced by suitable selection of conditions of monomolecular layer formation, for example, the concentration of hydrogen ions in the aqueous phase, species of ions, and the surface pressure.

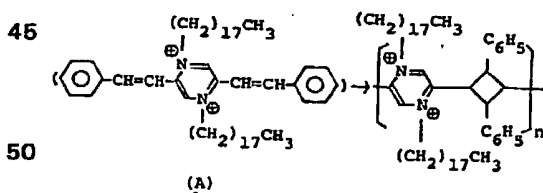
Formation of a protective film on the monomolecular film or the built-up film of monomolecular layers is favourable for the purpose of improving the chemical stability of the film, but the protective film is not always necessary depending upon the monomer to be used.

The invention is illustrated in more detail with reference to the following preparation and application examples.

#### Example 1

A quaternary salt **A** prepared by introducing an n-octadecyl group on the pyrazine ring of 2,5-distyrylpyrazine was used as monomer for film formation. While keeping the surface pressure constant, the monomolecular film and built-up films of 5, 10, 20, 30, 50, 70, and 100 monomolecular layers were transferred on clean hydrophilic surfaces of glass substrates according to the vertical dipping method, thereby preparing optical recording media. In the formed films, the monomer molecules oriented with the pyrazine rings directing toward the substrate.

Optical recording media thus prepared were irradiated with an X-ray according to a pattern to cause the polymerization as shown in the following equation (VI), thereby recording information.



(perchlorate ions dissolve in the water during formation of the film).

Using these optical recording media, particularly those having built-up films of 5–70 monomolecular layers, high density recording of the order of molecular dimensions could be achieved.

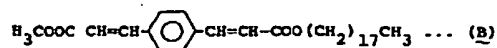
Information recorded in these recording media could be read out with high S/N ratios by using a beam of visible light having a wavelength of 420 nm.

The information recorded in these optical recording media was erased by heating the media to 300°C. Then, information was recorded again in the media by X-ray irradiation according to a pattern.

Thus, high density recording of the order of molecular dimensions was possible with the optical recording media and that repeatedly.

#### 65 Example 2

Using compound B:



- 5 as a monomer for film formation, the same operation as in Example 1 for transferring a monomolecular film onto each of substrates was repeated to prepare built-up films of 10, 20, 50, 100, 200, 300, 400, and 500 monomolecular layers. 5
- 10 Optical recording thus media prepared were irradiated with ultraviolet rays according to a pattern to cause polymerization at the irradiated sites, thereby recording information. 10
- Information recorded in the media could be read out successfully, particularly from built-up films of 10 to 100 monomolecular layers, by detecting the specific volume difference between the monomer and the polymer according to a schlieren method.
- 15 In addition to high density recording and good reproduction, repeated use of the optical recording media was possible similarly to those of Example 1. 15

### Example 3

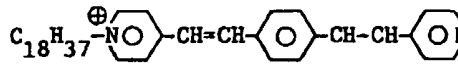
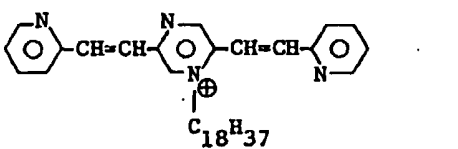
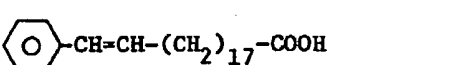
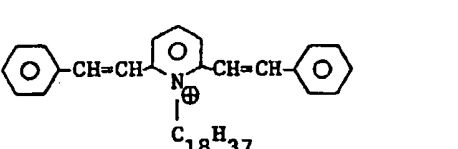
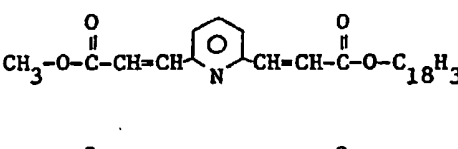
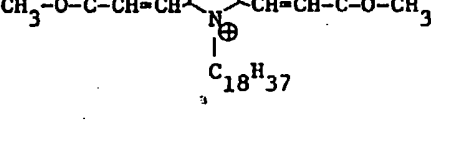
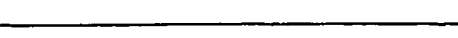
In the same manner as in Example 1, optical recording media were prepared by using photopolymerizable monomers shown in Table 1.

Table 1

5	Photopolymerizable monomer for forming the film	Number of mono-molecular layers in built-up film	5
10	$C_{18}H_{37}^{\oplus}-N \text{ (pyridine ring) } -CH=CH-\text{C}_6\text{H}_4-CH=CH-\text{C}_5\text{H}_4\text{N}$	5	10
15	$\text{C}_5\text{H}_4\text{N}-CH=CH-\text{N}^{\oplus} \text{ (pyridine ring) } -CH=CH-\text{C}_5\text{H}_4\text{N}$ $ $ $C_{18}H_{37}$	10	15
20			20
25	$\text{C}_6\text{H}_5-CH=CH-(CH_2)_{17}-COOH$	10	25
30	$\text{C}_6\text{H}_5-CH=CH-\text{N}^{\oplus} \text{ (pyridine ring) } -CH=CH-\text{C}_6\text{H}_5$ $ $ $C_{18}H_{37}$	10	30
35	$CH_3-O-C(=O)-CH=CH-\text{N} \text{ (pyridine ring) } -CH=CH-C(=O)-O-C_{18}H_{37}$	20	35
40	$CH_3-O-C(=O)-CH=CH-\text{N}^{\oplus} \text{ (pyridine ring) } -CH=CH-C(=O)-O-CH_3$ $ $ $C_{18}H_{37}$	20	40
45			45
50	$CH_3-(CH_2)_{11}-C \equiv C-C \equiv C-(CH_2)_8-COOH$	20	50

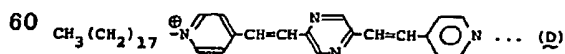
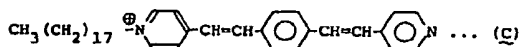
Recording and reproducing tests were conducted on the optical recording media thus prepared by using the rays shown in Table 2. With all the media, high density recording of the order of molecular dimensions was possible and these media could be used repeatedly by heating them after recording, similarly to Example 1.

Table 2

5	Photopolymerizable monomer for forming the film	Writing Ray	Reading method	5
10		UV-rays	Visible ray ( $\lambda = 450 \text{ nm}$ ) Schlieren method	10
15		X-ray	Visible ray ( $\lambda = 450 \text{ nm}$ ) Schlieren method	15
20		UV-rays	Visible ray ( $\lambda = 420 \text{ nm}$ ) Schlieren method	20
25		X-ray	Visible ray ( $\lambda = 460 \text{ nm}$ ) Schlieren method	25
30		X-ray	Schlieren method	30
35		X-ray	Schlieren method	35
40		X-ray	Schlieren method	40
45				45
50				50

**Example 4**

Built-up films of monomolecular layers were formed on glass substrates by using the following monomers **C** and **D** in combination as film components.



A solution of **C** in chloroform was extended on a water surface to form a monomolecular layer of **C** thereon. Similarly a solution of **D** in chloroform was extended on a water surface in another vessel, to form a monomolecular layer of **D**. While keeping the surface pressure constant, a

glass substrate having a sufficiently cleaned and hydrophilic surface was gently sunk into the C-supporting water and a part of the monomolecular film of C was transferred onto the substrate. Then the substrate was sunk into the D-supporting water and a part of the monomolecular film of D was transferred onto the monomolecular film already transferred onto the substrate. By repeating these transfer operations, optical recording media having recording layers of 50–3000 Å in thickness were prepared. 5

Information was recorded in the optical recording media thus prepared, by X-ray irradiation according to a pattern. Recorded information could be read out with high S/N ratios in particular from the recording layers 300–3000 Å thick by using a visible ray of wavelength 420 nm. 10

These recording media were heated to 350°C to remove recorded information, and were subjected again to X-ray pattern irradiation to record information.

Thus, high density recording of the order of molecular dimensions was possible with the optical recording media and that repeatedly. 15

#### Example 5 15

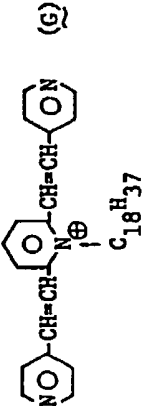
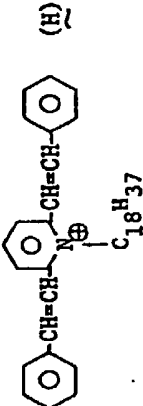
In the same manner as in Example 4, optical recording media were prepared by using the combination of photopolymerizable monomers shown in Table 3.

Recording and reproducing tests were conducted on the optical recording media thus prepared, by using the rays shown in Table 3. With all the media, high density recording of the order of molecular dimensions was possible and these media could be used repeatedly by heating them after recording, similarly to Example 4. 20

Table 3

Photopolymerizable monomer for forming the film	Film structure	Schematic diagram of film structure	Writing ray	Reading method
$\text{CH}_3\text{-O-C(=O)-CH=CH-}\langle\bigcirc\rangle\text{-CH=CH-C(=O)-C}_{18}\text{H}_{37} \quad (\text{E})$ $\text{CH}_3\text{-O-C(=O)-CH=CH-}\langle\bigcirc\text{N}\rangle\text{-CH=CH-C(=O)-C}_{18}\text{H}_{37} \quad (\text{F})$	<p>Lower 5 layers (substrate side) consisted of <math>\text{E}</math>.</p> <p>Upper 5 layers consisted of <math>\text{F}</math>.</p> <p>10 layers in all.</p>		X-ray	Visible ray $\lambda = 420 \text{ nm}$
$\text{E}$ and $\text{F}$	<p>Lower 10 layers consisted of <math>\text{E}</math>.</p> <p>Upper 10 layers consisted of <math>\text{F}</math>.</p> <p>20 layers in all.</p>		X-ray	Visible ray $\lambda = 420 \text{ nm}$
$\text{E}$ and $\text{F}$	$\text{E}$ and $\text{F}$ layers were cumulated alternately in that order from the substrate side. 20 layers in all.		X-ray	Visible ray $\lambda = 420 \text{ nm}$ Schlieren method

Table 3 (continued)

 <p>(G)</p>	<p>Lower 10 layers consisted of <math>\tilde{G}</math>.</p> <p>Upper 10 layers consisted of <math>\tilde{H}</math>.</p> <p>20 layers in all.</p>	<p>10 layers</p> <p><math>\tilde{H}</math></p> <p>10 layers</p> <p><math>\tilde{G}</math></p> <p>10 layers</p> <p><math>\tilde{H}</math></p> <p>Substrate</p>	X-ray	Visible ray $\lambda = 450 \text{ nm}$
 <p>(H)</p>	<p>Lower 10 layers consisted of <math>\tilde{H}</math>.</p> <p>Upper 10 layers consisted of <math>\tilde{G}</math>.</p> <p>20 layers in all.</p>	<p>10 layers</p> <p><math>\tilde{G}</math></p> <p>10 layers</p> <p><math>\tilde{H}</math></p> <p>10 layers</p> <p><math>\tilde{H}</math></p> <p>Substrate</p>	X-ray	Visible ray $\lambda = 450 \text{ nm}$



## CLAIMS

1. An optical recording medium comprising one or more distributed photopolymerisable monomers arranged to produce an erasable, image-readable pattern of localised polymer areas upon image-wise irradiation.
- 5 2. An optical recording medium according to claim 1 in which the or each monomer is arranged in one or more monomolecular layers.
3. An optical recording medium according to claim 2 in which the molecules in each layer have a common orientation.
4. An optical recording medium according to any preceding claim in which the or each monomer comprises a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule.
- 10 5. An optical recording medium according to claim 4 wherein at least one of the said monomers is represented by the general formula:
 
$$15 \quad R_1-CH=CH-R_2 \quad 15$$

where (1) a hydrophilic site and a hydrophobic site are both present in  $R_1$  or (2) in  $R_1$  and  $R_2$  or (3)  $R_1$  is hydrophobic relative to  $R_2$ .

- 6. An optical recording medium according to claim 4 wherein at least one of the said monomers is represented by the general formula:
 
$$20 \quad R_1-CH=CH-R_3-CH=CH-R_2 \quad 20$$

where (1) one of  $R_1$ ,  $R_2$ , and  $R_3$  contains a hydrophilic site and a hydrophobic site or (2) one of  $R_1$ ,  $R_2$ , and  $R_3$  is hydrophobic relative to the remainder and one of the remainder is hydrophilic.

- 7. An optical recording medium according to claim 4 wherein at least one of the said monomers is represented by the general formula
 
$$30 \quad R_1-C\equiv C-C\equiv C-R_2 \quad 30$$

where (1) a hydrophilic site and a hydrophobic site are both present in  $R_1$  or (2) in  $R_1$  and  $R_2$  or (3)  $R_1$  is hydrophobic relative to  $R_2$ .

- 8. An optical recording medium according to any preceding claim comprising a said photopolymerisable monomer which has at least one unsaturated bond and at least one  $C_{10}-C_{30}$  long chain alkyl group.
- 9. An optical recording medium according to any preceding claim comprising a recording layer which is built-up film of monomolecular layers formed on a substrate, of two or more kinds of photopolymerisable monomers having a hydrophilic group, a hydrophobic group, and at least one unsaturated bond in the molecule respectively.
- 10. A recording medium substantially as described herein with reference to any one of compounds 1 to 38.
- 11. A recording medium substantially as described herein with reference to any one of the Examples.
- 12. An optical recording process in which the recording medium comprises one or more distributed photopolymerisable monomers and in which image-wise irradiation induces a polymerisation reaction in the irradiated areas leading to the detectable localised presence of polymer.
- 13. A process according to claim 12 in which there is utilised a recording medium according to any of claims 1 to 11.
- 14. A process according to claim 12 or claim 13 in which the recording is carried out with Y, X, or ultraviolet radiation.
- 15. A process according to any of claims 12 to 14 in which image reproduction is carried out with visible radiation.
- 16. A process according to any of claims 12 to 15 in which a change in light absorbance is utilised to detect the localised presence of polymer.
- 17. A process according to any of claims 12 to 15 in which a localised volume change is utilised to detect the presence of polymer.
- 18. A process according to any of claims 12 to 17 in which the recorded image is erasable.
- 19. A process according to claim 18 in which erasing is carried out by heat.
- 20. A process according to claim 19 in which to erase the image, the recording medium is heated to a temperature from 300°C to 450°C.
- 21. A process according to claim 12 substantially as described herein with reference to the accompanying drawings.
- 22. An optical recording process substantially as described herein with reference to any of the Examples.
- 23. Any one of compounds 1 to 38 as specified hereinbefore.

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